Effect of nitro-functionalization on the cross-linking and bioadhesion of biomimetic adhesive moiety

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SUPPORTING INFORMATION

Tensile testing of bovine pericardium substrates

Mechanical properties of bovine pericardium substrates were determined using uniaxial tensile testing (ElectroForce® 3200 Series III Test Instruments, Bose, Eden Prairie, MN). Pericardium tissues were equilibrated in 10 mM sodium phosphate buffer adjusted to a pH of 5.7, 6.7, 7.4, or 8.0 and cut into strips (width ~ 5 mm, thickness ~ 0.6 mm). The dimensions of each sample were measured using a digital caliper immediately before testing. The initial length between two tensile grips was fixed at 11.45 mm and the samples (n = 4) were pulled at a rate of 5 mm/min until failure. Stress was determined based on the measured load divided by the initial cross-sectional area of the sample. Strain was determined by dividing the change in the position of the tensile grip by 11.45 mm. The elastic modulus was taken from the slope of the linear portion of the stress-strain curve.

Table S1. Tensile properties of pericardium tissue used as the model tissue substrate for adhesion testing.

pH	5.7	6.7	7.4	8.0
Failure Strength (kPa)	8,850 ± 1560	8,450 ± 1250	8,460 ± 590	9,180 ± 1,480
Failure Strain	0.50 ± 0.070	0.49 ± 0.090	0.66 ± 0.061	0.37 ± 0.050*
Elastic Modulus (kPa)	31,400 ± 8,570	26,700 ± 9,800	21,800 ± 7,160	28,658 ± 7,020

***** statistically different from other pH levels based on ANOVA ($p < 0.05$)

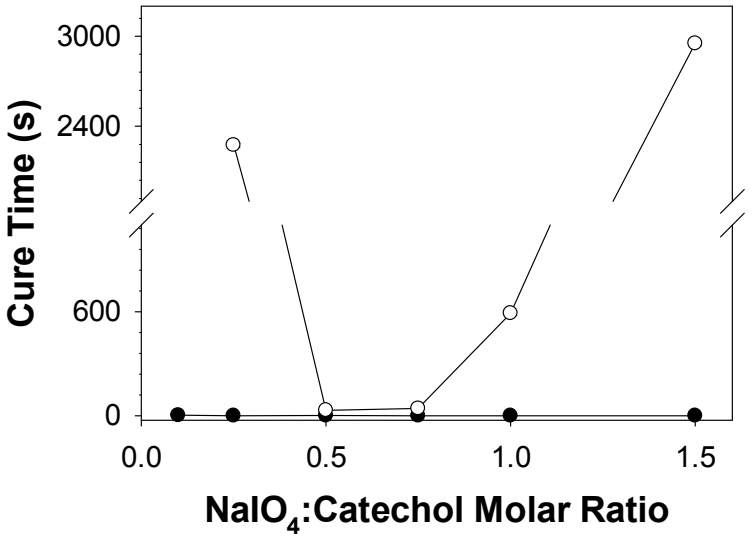


Figure S1. Cure time of PEG-ND (●) and PEG-D (○) as a function of $NaIO_4$:catechol molar ratio for hydrogels formulated with precursor solutions adjusted to a pH of 7.4. Data for PEG-D was obtained from published report.[1]

Table S2. Equilibrium swelling ratio of hydrogels after incubation in sodium phosphate buffer (pH = 7.4) for 24 hrs*

IO_4:nitrodopamine molar ratio	pH 5.7	pH 6.7	pH 7.4	pH 8
0.1	1.8±0.40	2.6±0.70	2.2±0.70	2.1±0.82
0.25	1.6±0.32	2.2±0.34	2.5±0.81	1.9±0.12
0.5	2.1±0.17	2.6±0.38	2.4±0.18	2.6±0.51
0.75	2.6±0.35	3.3±0.94	2.4±0.19	2.4±0.16
1	2.4±0.19	3.1±0.12	2.5±0.14	2.8±0.16
1.5	2.2±0.05	5.2±2.2	2.9±0.06	3.0±0.16

* Calculated as a ratio between the volumes of the swollen (V_s) and relaxed (V_r) hydrogel

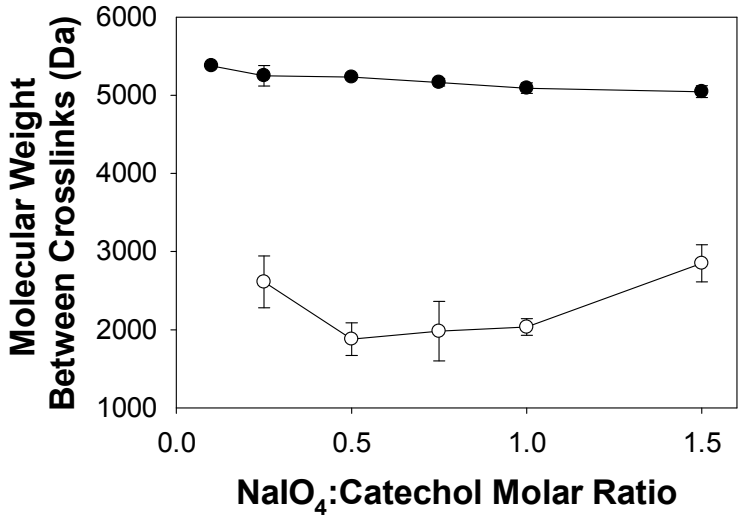
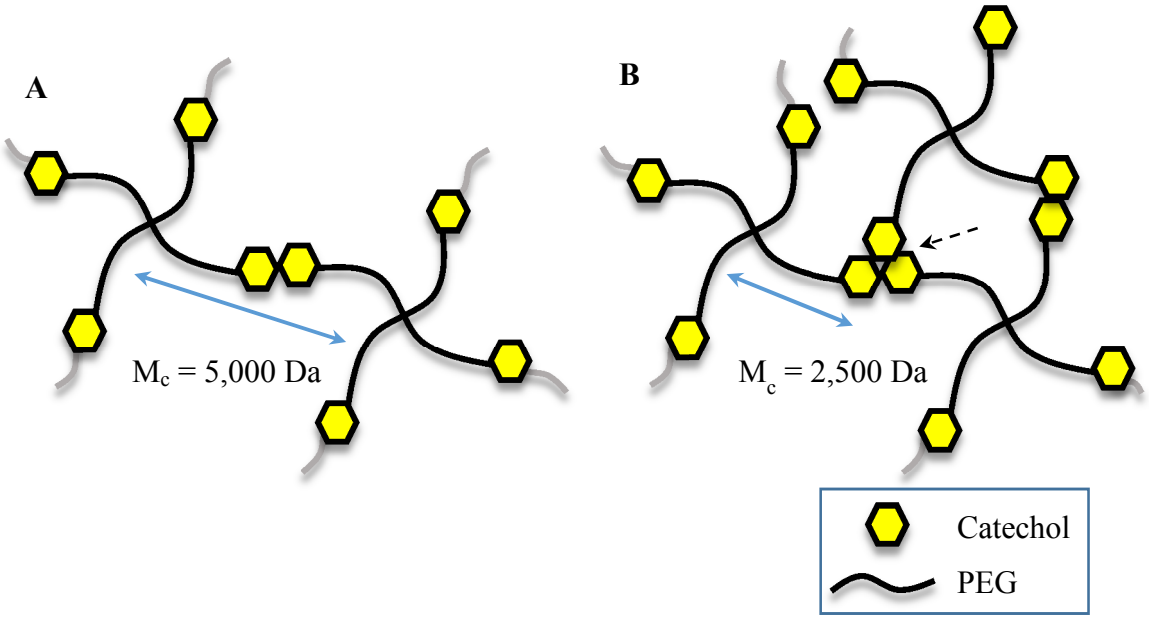
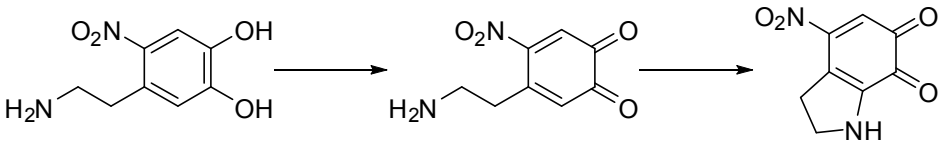


Figure S2. Molecular weight between crosslinks for PEG-ND (●) and PEG-D (○) as a function of $NaIO_4$:catechol molar ratio for hydrogels formulated with precursor solutions adjusted to a pH of 7.4. Data for PEG-D was obtained from published report.[1]



Scheme S1. Schematic representation of idealized network after terminal catechol groups formed dimer (**A**) and trimer (**B**). The formation of the trimer forms a new junction point (dashed arrow in **B**), which reduces the molecular weight between crosslinks (M_c; double-sided arrows).



Scheme S2. Formation of oxidation intermediate of nitrodopamine through intramolecular cyclization.

Table S3. Adhesive properties of PEG-ND, PEG-D and commercial CoSeal tested at pH 7.4

	PEG-ND	**PEG-D**	**CoSeal**
Adhesive Strength (kPa)	3.7±1.0	7.8±1.7	0.63±0.19

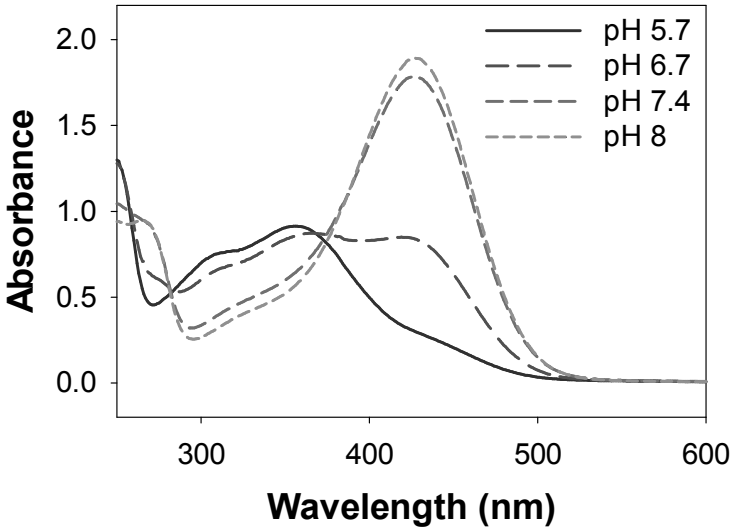


Figure S3. UV-vis spectrum of 50 μM of PEG-ND (200 μM of nitrodopamine) buffered at different pH levels.

References

1. Cencer, M. M.; Liu, Y.; Winter, A.; Murley, M.; Meng, H.; Lee, B. P. *Biomacromolecules* **2014,** *15*, 2861–2869.